

Rec'd PCT/PTO 28 FEB 2005

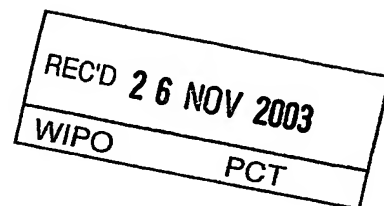
20/525939 #2

PCT / IN 03 / 00278 1

**PRIORITY
DOCUMENT**

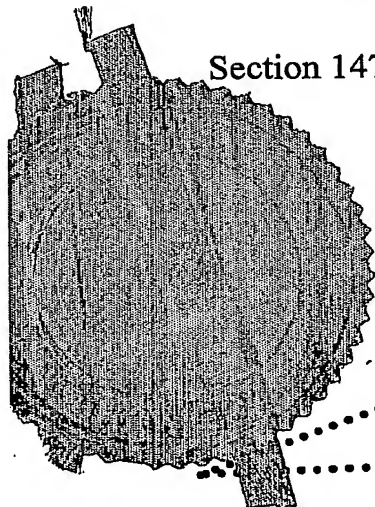
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

THE PATENTS ACT, 1970



IT IS HEREBY CERTIFIED THAT, the annex is a true
copy of Application & complete specification filed on 29.08.2002 in
respect of Patent Application No. 783/MUM/2002 of Tata Institute of
Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400 005,
State of Maharashtra, India, an aided autonomous institution under the
administrative purview of Atomic Energy, Government of India.

This certificate is issued under the powers vested in me under
Section 147 (1) of the Patents Act, 1970.

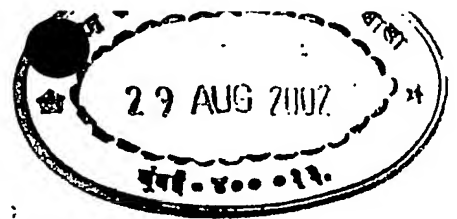


.....
Dated this 6 / 11 day of November 2003

M. A. Haafiez.

(M.A. HAAFEEZ)

ASST. CONTROLLER OF PATENTS & DESIGNS



FORM 1
THE PATENTS ACT, 1970
APPLICATION FOR GRANT OF A PATENT (Section 5(2), 7 and Rule 33A)
(IN TRIPLICATE)

We, TATA INSTITUTE OF FUNDAMENTAL RESEARCH, Homi Bhabha Road, Colaba, Mumbai 400 005, State of Maharashtra, India, an aided autonomous institution under the administrative purview of Atomic Energy, Government of India.

1. hereby declare -

(a) that we are in possession of an invention titled A Process For Manufacture Of Half Metallic Ferromagnet CrO_2 Or Composites Of $\text{CrO}_2/\text{Cr}_2\text{O}_3$

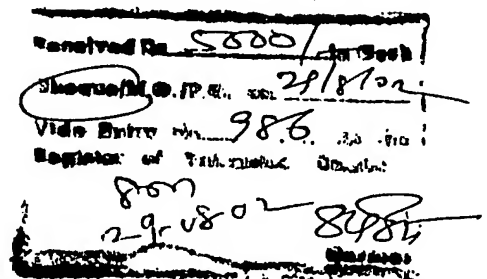
(b) that the Provisional/ Complete Specification relating to this invention is filed with this application.

(c) that there is no lawful ground of objection to the grant of a patent to us.

2. further declare that the inventors for the said invention are

a) Dr. Ashna Bajpai,
Visiting Fellow,
Department of Condensed Matter Physics
Tata Institute of Fundamental Research,
Homi Bhabha Road, Mumbai 400 005

b) Prof. Arun Kumar Nigam
Associate Professor (G),
Department of Condensed Matter Physics
Tata Institute of Fundamental Research,
Homi Bhabha Road, Mumbai 400 005



3. We claim the priority from the application(s) filed in convention countries, particulars of which are as follows : NONE.

4. We state that the said invention is an improvement in or modification of the invention, the particulars of which are as follows and of which we are the applicant/patentee : NOT APPLICABLE.

5. We state that the application is divided out of our application, the particulars of which are given below and pray that this application deemed to have been filed on _____ under section 16 of the act : NOT APPLICABLE.

6. that we are the assignee of the true and first inventor

7. that our address for service in India is as follows ; C/o Mr. Majumdar, M/s S. Majumdar & Co Patent & Trade Marks Attorneys, 5, Harish Mukherje Road, Calcutta-700025.

783/MUM/2002
29/8/2002

783/मुंबई/2002
MUM
29 AUG 2002

ORIGINAL

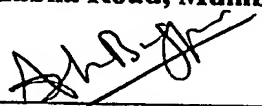
8. We, the true and first inventor for this invention declare that the applicant herein is our assignee


a) Dr. Ashna Bajpai,
Visiting Fellow,
Department of Condensed Matter Physics
Tata Institute of Fundamental Research,
Homi Bhabha Road, Mumbai 400 005

b) Prof. Arun Kumar Nigam
Associate Professor (G),
Department of Condensed Matter Physics
Tata Institute of Fundamental Research,
Homi Bhabha Road, Mumbai 400 005



(Signed)


(Ashna Bajpai)


(Arun Kumar Nigam)

9. that to the best of our knowledge, information and belief the fact and matters stated herein are correct and that there is no lawful ground of objection to the grant of patent to us on this application.

10. following are the attachments with the application

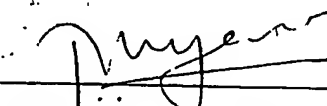
- (a) ~~provisional~~/complete specification (in triplicate)
- (b) abstract of the invention (in triplicate)
- (c) drawings, (in triplicate)
- (d) fee Rs. 5000.00 (five thousand rupees only) in bank draft bearing no. 052455 dated 28/8/02 drawn on standard chartered Bank.

We request that a patent may be granted to us for the said invention

Dated this 28th day of August 2002.

The Controller of patents
The patents Office
Mumbai.

(Signed)


Dr. J. N. Kayastkar
REGISTRAR

TATA INSTITUTE OF FUNDAMENTAL RESEARCH
HOMI BHABHA ROAD, MUMBAI-400 005

FORM 2

**THE PATENTS ACT 1970
COMPLETE SPECIFICATION**

(See Section 10)

TITLE

**A Process For Manufacture Of Half Metallic Ferromagnet
CrO₂ or Composites Of CrO₂/Cr₂O₃**

APPLICANT

**Tata Institute of Fundamental Research,
Homi Bhabha Road, Colaba, Mumbai 400 005, Maharashtra, India.
An aided autonomous institution under the administrative purview of the
Department of Atomic Energy, Government of India,
Anushakti Bhavan, Chatrapati Shivaji Maharaj Marg,
Mumbai 400 005, Maharashtra, India.**

ORIGINAL

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

7 83 | मुंबई | 2002
MUM

29 AUG 2002

Field of invention:

The present invention relates to a process for manufacture of half-metallic ferromagnet either substantially pure chromium dioxide (CrO_2), or composites of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$).

The present invention particularly relates to a simple process for manufacture of ferromagnetic chromium dioxide (CrO_2) from chromium trioxide (CrO_3), as well as a composite of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$) via an intermediate oxide Cr_8O_{21} .

Background and Prior Art:

B.L Chamberland has reviewed in 1977 "The chemical and physical properties of CrO_2 and tetravalent chromium oxide derivatives" in *CRC Critical Rev in Solid State and Mater. Sci.* 7, 1 (1977). Chromium dioxide (CrO_2) is a metallic, room temperature ferromagnet with Curie temperature (T_c) around 385 K. It stabilizes in tetragonal Rutile structure, Space Group $P4_2/\text{mm}$. In this compound, Cr is in 4^+ state contributing 2 μ_B per Cr atom in the system. Its known to show the metallic conductivity in single crystals and epitaxially grown thin films. However, activated behavior is seen in polycrystalline CrO_2 , that is believed to be arising from hopping of the charge carrier across grain boundaries in polycrystals. JMD Coey et.al, have related this mechanism of conduction to the origin of large magnetoresistance exhibited by CrO_2 in their paper entitled "Magnetoresistance of Chromium dioxide powder compacts, *Phy. Rev. Lett.* 80, 3815, 1998". Recently in 2001, Ji et.al, have observed, through Andreev reflection measurements, the maximum spin polarization close to 100% in CrO_2 , vis a vis other materials showing half metallicity *Phy. Rev. Lett.* 86, 5585, 2001.

The ferromagnetic sample is characterized by its saturation magnetization M_s at 0 K and Curie temperature T_c . The theoretical values for saturation magnetization for CrO_2 is about 135 emu/gm. The best reported value for the saturation magnetization for polycrystalline samples range from 75 –87 emu/gm (Table 2). The single crystals have shown value of the order of 108 emu/gm whereas epitaxial thin films of high quality have

shown M_s close to the theoretical values. For instance, Li et.al have reported in *Appl. Phy. Lett*, 75, 713, 1999, M_s value of the order of 135 emu/gm for a 4000Å thick CrO_2 films.

It is known in literature that sintering of CrO_2 is difficult since it is a metastable phase and easily converts to Cr_2O_3 even at modest temperatures of 200°C. (F.Y. Yang et.al, *Appl. Phys. Lett.*, 77, 286, 2000).

The ferromagnetic CrO_2 is used as a particulate media in recording industries. As mentioned earlier, CrO_2 has been found to be a half metallic ferrimagnet with nearly full spin polarization. Recently, the half-metallic ferromagnets, as a magnetoresistive material have been employed in various magneto-electronic applications. One area in which half metallic ferromagnets have tremendous device application is Magnetic Tunnel Junctions. (Warren E Picket and Jagdeesh S Moodera, "Half-metallic Magnets" *Physics Today*, May 2001).

The presence of even a small amount of impurity phase not only affects the ferromagnetic properties but also interferes with the phenomenon of half metallicity / spin polarization severely. This results in the loss of spin polarization and thus bringing down the efficiency of the concerned device, based on spin polarized current.

Since CrO_2 is a material of industrial importance, there have been a large number of patents and papers on various preparation methods and intricacies involved for preparing CrO_2 . The related prior art is presented in Table 1.

Since the saturation magnetization value (M_s) is an important criteria for a pure ferromagnetic material, and is a test for comparing various processes, some M_s values from literature for CrO_2 are given in Table 2.

Table 1.

US Patent	Starting Material	Temp. Pressure	Product	Remarks
2923685 (1960)	CrO ₃ , H ₂ O, Na ₂ SO ₄	450°C, 1000 Atm	CrO ₂	*
3423320 (1969)	KCr ₃ O ₈ , H ₂ O,	2600 Atm	CrO ₂	needle like FM
3449073 (1969)	CrO ₃ , Cr ₂ O ₃ , Na ₂ Cr ₂ O ₇	850 Atm	CrO ₂	fine grain particles
4428852 (1984)	preheated hydrated chromium oxide	elevated pressure/ continuous process	CrO ₂	*
3117093 (1964)	Cr _x O _y 2y/x is 4 - 5.5	50 - 3000 Atm	CrO ₂	*
3493338 (1970)	CrO ₃ , NO, O ₂	225, 325 °C no pressure	CrO ₂ 94%+ CrO ₃ , 5%	*
5856008 (1999)	CrO ₃	520 °C 35000 bar	CrO ₂ CrO ₂ coated with Cr ₂ O ₃	* **

- relevant to production of CrO₂ ; * * relevant to production of CrO₂ / Cr₂O₃ Composite.

Table 2: Saturation Magnetization Values for CrO₂

Reference	Saturation Magnetisation (M _s) (emu/gm)
Theoretical Value of M _s	~135
US Patent 4747974 (polycrystal)	75-78
US Patent 3493338 (polycrystal)	24-84 (including modifier)
US Patent 3486851 (polycrystal)	78-87
US Patent 3451771 (polycrystal)	21-35
US Patent 2923683 (polycrystal)	38-66 (with modifier)
Poly crystal Chamberland (1977)	73-75
Single crystal and Epitaxial films (Chamberland 1977)	100
4000 Å thick film (Li, Gupta and Xiao 1999)	~133

Table 1 shows that

- (a) CrO_3 (chromium VI oxide) has been used as a starting material. CrO_2 can be prepared by thermal decomposition of CrO_3 and mixed chromium oxides.
- (b) There exist a very narrow window of temperature and pressure in which many other oxides of chromium stabilize, including CrO_2 , and the phase boundary between these oxides is very fuzzy. Consequently a little variation in preparation condition results in mixed phase or impure compounds Chamberland has discussed this aspect by showing it in Figs.1 and 2 on page 3 of his review (*ibid.*).
- (c) The difficulties of accurately measuring and controlling pressure, along with the fact that it requires expensive high-pressure assemblies leading to high production cost are the main drawbacks of above mentioned preparative methods. It is desirable to have a preparative method, which does not need pressure as controlling parameter.
- (d) The last three US patents in the above table form relevant prior art to the present invention and will be discussed after describing the present invention in detail.

Object

The main object of the present invention is to provide a method for manufacture of either half-metallic ferromagnet chromium dioxide (CrO_2), or composites of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$) that does not require pressure as a control parameter and that does not result in any additives in the product.

Summary of the Present Invention:

Thus according to the present invention there is provided a process for manufacture of substantially pure half metallic ferromagnet chromium dioxide (CrO_2), or composites of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$) comprising heating Cr_8O_{21} to a temperature of between 350 and 480°C for a period of between 1-5 hours whereby substantially pure chromium dioxide (CrO_2), or composites of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$) are formed.

Detailed Description of the Present Invention.

Thus the process of present invention comprises the following reactions

A $\text{Cr}_8\text{O}_{21} \rightarrow \text{CrO}_2$ or composite $\text{CrO}_2 / \text{Cr}_2\text{O}_3$ by heating at $350-480^\circ\text{C}$.

A1 $\text{Cr}_8\text{O}_{21} \rightarrow \text{CrO}_2$ by heating at $350-400^\circ\text{C}$;

A2 $\text{Cr}_8\text{O}_{21} \rightarrow$ composite $\text{CrO}_2 / \text{Cr}_2\text{O}_3$ by heating at $400-480^\circ\text{C}$].

According to the above process, when temperature is maintained between 350°C and 400°C CrO_2 is formed as the product (Step A1) and when the temperature is between 400°C to 480°C it gives $\text{CrO}_2 / \text{Cr}_2\text{O}_3$ composite (Step A2).

In step A it is preferred to maintain the temperature of Cr_8O_{21} in the specified range for 2-3 hours. To convert Cr_8O_{21} to substantially pure CrO_2 according to step A1 it is preferred to maintain the temperature range between $390-400^\circ\text{C}$ and to convert Cr_8O_{21} to the said composite of chromium dioxide and chromium sesquioxide ($\text{CrO}_2 / \text{Cr}_2\text{O}_3$) according to step A2 the temperature range should be preferably maintained between $400-450^\circ\text{C}$.

According to a preferred aspect Cr_8O_{21} is prepared from CrO_3 by heating the latter and maintaining the temperature from $220-330^\circ\text{C}$ for 6 to 14 hours, preferably for 8-12 hours. It is further preferred to maintain a temperature in the range of $250-280^\circ\text{C}$.

CrO_3 is taken in an inert container and heated slowly to raise the temperature to about 250°C and thereafter maintained in the temperature range from $250-280^\circ\text{C}$, for about 8-12 hours in dry oxygen/air at about atmospheric pressure, till it is converted to Cr_8O_{21} as characterized by X ray diffraction. Thereafter it is cooled to room temperature at the same rate as that used for raising the temperature initially.

The product so formed is crushed in any inert vessel to form a powder and then the powder is sealed in a glass tube of inert material. The powdered can also be palletized before sealing it in the inert tube. Thereafter the tube is placed in a preheated furnace maintained at a temperature in the range of about $390-450^\circ\text{C}$ for about 2-3 hours till it is converted to said half-metallic ferromagnet viz. said substantially pure chromium

dioxide CrO_2 when at 350 - 400°C or a composite of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$) when at 400 - 450°C, as characterized by XRD.

The sealed tube is then opened after cooling it to ambient temperature and the contents are stored in any dry container.

After lot of experimentation we have found that the stoichiometry of the final product at a certain temperature depends on the quality of precursor. It is found that stoichiometric CrO_2 can be prepared even if oxygen flow was not maintained while making Cr_8O_{21} . It is preferable to maintain the oxygen flow else a slight variation in preparation temperature leads to the formation of other oxides of chromium, which may adversely effects, the quality of CrO_2 .

US patent 3,493,338 there is only one step reaction: $\text{CrO}_3 \rightarrow \text{CrO}_2$. There is no isolation of the intermediate product. Heat treatment cycle is as follows: RT \rightarrow 175 °C in 10 min. \rightarrow 225 °C in 1 hour \rightarrow 325 °C in 20 min. and maintained at 325 for 2 hrs. All the while there is gas (- a mixture of 3.5 % NO and O_2) flow at normal atmospheric pressure is run over the boat carrying CrO_3 at about 200 cc /min. The M_s value of the CrO_2 obtained is ~ 84 emu/g; where as that in the present process product is ~ 125 emu/g.

The US patent 3,117,093 describes two step process, the second step starting with Cr_xO_y with average chromium valance ratio ($2y/x$) of 4.2 - 4.3 which is 5.25 for Cr_8O_{21} used in the process of present invention. This is mixed with water and other modifiers such as antimony sesqui oxide inside a platinum tube and reaction carried out under a pressure of 50 - 3000 Atm. There are, however 3 examples (No.14, 15 and 16) in this patent, which describe the process without any modifier. The first step starts with chromic nitrate nonahydrate; it is heated at 330 °C for 2 hours to obtain an intermediate chromium oxide Cr_xO_y not a well-defined compound as said above. In these three examples the reaction $\text{Cr}_x\text{O}_y \rightarrow \text{CrO}_2$ was carried out at 400 °C for 1 to 2 hours. This starting material Cr_xO_y was either moist 3 - 9 % moisture or taken water for milling before heat treatment. Though in these examples there is no mention about pressure, the reaction has been claimed to be done at from 50 - 3000 atmosphere pressure. It will be

clearly seen that the Step A of the present invention is different from this prior art. The starting material in step B of the present invention is different from this prior art. Step B in the present invention is in dry state, that in these examples without modifier in the US patent 3,117,093 is in the moist state. The temperature of the reaction at step B is 400°C at 750 atmosphere and 17% water, in the US patent 3,117,093. Conditions are therefore different in the present invention for production of CrO₂.

Thus the process of present invention is different from this prior art process.

In US patent 5,856,008 process, the reaction $\text{CrO}_3 \rightarrow \text{CrO}_2$ is done in a gold capsule at 35 k bar pressure at 520 °C for 2 hours in a piston cylinder type high pressure furnace; on cooling to room temperature the pressure is removed.

Thus this is a one step reaction different from the process of present invention. The CrO₂ thus obtained is annealed for 30 minutes in air at 380 °C, and another sample at 420 °C. And it is believed that in this process CrO₂ gets a surface coating of Cr₂O₃, based on XRD measurements.

In the process of present invention, $\text{CrO}_3 \rightarrow \text{Cr}_x\text{O}_{2x} \rightarrow \text{composite CrO}_2 / \text{Cr}_2\text{O}_3$ by heating at 400 - 450 °C, and is clearly different from US patent 5,856,008. The process of present invention for manufacture of composites is simpler and does not need pressure as a control parameter.

EXAMPLES

The invention will now be illustrated with the help of examples. The examples are by way of illustration only and in no way restrict the scope of the invention.

Equipment Used:

The equipment used in these examples is a tubular furnace (Carbolite model CTF12/65 furnace). The furnace has a temperature range up to 1200°C and has the arrangement for flow of inert or oxygen flow.

Inert containers used for reaction are chosen from quartz, Pyrex glassware.

Chemicals used:

CrO_3 granules with 99.9% purity were obtained from Aldrich Chemical company, USA.

Analytical Facilities used:

Siemens Diffractometer (Model D-500): for powder X-ray diffraction measurements (XRD).

Wave Dispersive Electron Probe Microanalyser (CAMECA Model EPMA SX-100): for scanning electron microscopy (SEM).

Vibrating Sample Magnetometer (Oxford MagLab VSM) and SQUID magnetometer (Quantum Design MPMS-XL7): for magnetization measurements.

Description of Figures in the accompanying drawings:

Fig. 1(a) - (d) : X-Ray diffraction pattern (2 θ vs Intensity) for the product of Examples I, II, III and IV respectively; the solid lines are fit to the experimental curve (circles).

Fig. 2: Scanning Electron Micrograph of the product of Example III. The long Needle shaped structures show the regular shape of CrO_2 particles.

Fig. 3. Magnetisation (M) as a function of magnetic field (H) for the product of Examples I, II., III and IV at 5 K.

Example I:

Chromium trioxide was taken in a quartz tube and it was heated slowly to raise the temperature to about 250 $^{\circ}\text{C}$, and thereafter the temperature was maintained at 250 $^{\circ}\text{C}$, for 10 hours under oxygen flow at about atmospheric pressure. The end product, Cr_8O_{21} after this reaction was a hard bar, which was crushed and powdered using agate mortar. This powder of Cr_8O_{21} (approx. 500 mg) obtained as above, was placed inside a Pyrex glass tube of 12 cm length and 1.5 cm diameter. The glass tube was sealed at atmospheric pressure and the ampoule was kept in a tube furnace at 392 $^{\circ}\text{C}$ for 2 hours.

X-ray diffraction, Rietveld refinement of powder XRD (R.A. Young et al Program DBWS-9411, 1994) was performed on this sample. The results are shown in Fig. 1(a). This product was therefore CrO_2 as evident from XRD pattern.

The powder was examined for the measurement of saturation magnetization on a SQUID magnetometer (Model MPMS-XL7 of Quantum Design, USA). At a temperature of 5K, this powder shows saturation magnetization (M_s) as large as 132 emu/gm, which is very close to the theoretically predicted value 135 emu/gm (E. P. Wohlfarth, Ferromagnetic Materials Vol.2, 471, 1980) [See Fig.3]. This proved that the CrO_2 product obtained at the end of Example I was a substantially pure material. For comparison, reported values of different ferromagnetic materials see Table 2. It will be seen that this is the only compound -the product of Example I - has the highest M_s value and it is very close to theoretical value.

Example II

The procedure of Example I was repeated, the only change being Cr_8O_{21} (1.5 g) was sealed inside a test tube of 1 cm diameter and 10 cm length. It was placed in the furnace at 392°C for 2 hrs. The final product was stoichiometric CrO_2 , and was identical with product of Example I in the above tests. The product of present invention is CrO_2 of polycrystalline type as confirmed by X-ray diffraction measurements, where no impurity peaks are observed (Fig 1(b)).

Example III

The procedure of Example I was repeated, the only change being Cr_8O_{21} (1.5 g) was ground for few hours and palletized in the form of a pellet of about 1.2 cm diameter and 0.2 cm thickness. This pellet was sintered at 250°C for few hours in tubular furnace. It was cooled to room temperature and was then sealed in a glass ampule at atmospheric pressure. This ampule was kept in the oven at 392°C for 2 hrs. The final product was a fairly hard pellet of stoichiometric CrO_2 .

The product of Example III was examined at room temperature under Scanning Electron Microscope (SEM). The SEM analysis was done on electron probe microanalysis (EPMA) system (model SX-100 from M/s CAMAC, France). The SEM picture is shown in Fig. 2, where long needle shaped grain are seen.

The X-ray diffraction measurement was done as in Example I and results are shown in Fig. 1(c).

The product of Example III was examined for the measurement of saturation magnetization (M_s) as in Example I. The results are shown in Fig. 3. The saturation magnetization is of the order of 125 emu/gm for this sample at 5 K (Table 1).

Example IV:

The procedure of Example I was repeated, with the only change of Cr_8O_{21} (1.5 g) sealed in a glass tube was kept in the oven maintained at temperature at around 425°C . The X-ray diffraction examination was done as in Example I and the results are shown in Fig. 1(d). The product formed was found to be a composite of $\text{CrO}_2/\text{Cr}_2\text{O}_3$ from XRD. The fraction of insulating Cr_2O_3 was also determined to be 45% (molar).

The product of Example IV was examined for M_s value, as in Example I. (See Fig. 3). The M_s value found to be 75 emu/gm at 5 K.

The M_s values obtained for Half-metallic FM materials obtained in these examples are given in Table 3.

Table 3 : M_s Values

Polycrystal example I, II	132 emu/g
Polycrystal example III	125 emu/g
Composite Example IV	75 emu/g at 5 K

Advantage of the present invention:

The process of present invention for manufacture of half metallic ferromagnet, high purity chromium dioxide (CrO_2), or composites of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$),

- i. does not need high pressure equipment, is simple to operate and is cost effective;
- ii. gives a polycrystalline CrO_2 in bulk, having saturation magnetization value nearer to that in epitaxial thin films and at a temperature of 5 K close to the theoretical value;
- iii. gives the final product in desired shape of fairly good hardness, required for all practical purposes such as for measuring electrical resistivity etc.;
- iv. provides CrO_2 of substantially high purity for spintronic devices.

We claim

1. A process for manufacture of half metallic ferromagnet, substantially pure chromium dioxide (CrO_2), or composites of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$) comprising heating Cr_8O_{21} to a temperature of between 350 and 480°C for a period of between 1-5 hours whereby substantially pure chromium dioxide (CrO_2), or composites of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$) are formed.
2. A process as claimed in claim 1, wherein Cr_8O_{21} is converted to said half-metallic ferromagnet substantially pure chromium dioxide CrO_2 when the temperature is maintained between 350 - 400°C or to a composite of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$) when the temperature is maintained between 400 - 480°C ;
3. A process as claimed in claim 1, wherein Cr_8O_{21} used in the process of the invention is prepared by heating CrO_3 and maintaining the temperature in the range of 230 - 320°C , preferably in the range 250 - 280°C ;
4. A process as claimed in claim 1 to 4, wherein said CrO_3 is heated and maintained in the said temperature range for 6-14 hours, preferably 8-12 hours;
5. A process as claimed in any one of the preceding claims, wherein CrO_3 is heated in dry oxygen/air;
6. A process as claimed in any one of the preceding claims, wherein CrO_3 is heated at about atmospheric pressure;
7. A process as claimed in any one of the preceding claims, wherein CrO_3 is heated slowly to raise the temperature to about 230°C and then maintained in the said temperature range;
8. A process as claimed in claim 1, wherein Cr_8O_{21} formed is cooled slowly to room temperature substantially at the same rate as it was heated.

9. A process as claimed in claim 1, wherein Cr_8O_{21} is crushed powder form;
10. A process as claimed in any of the preceding claims, wherein the said Cr_8O_{21} powder is sealed in a tube or can be palletized and sintered before sealing in a tube;
11. A process as claimed in any one of the preceding claims, wherein the temperature of Cr_8O_{21} is maintained in the said range for 2-3 hrs;
12. A process as claimed in any one of the preceding claims, wherein Cr_8O_{21} is converted to said substantially pure chromium dioxide CrO_2 when the temperature is maintained between $390-400^\circ\text{C}$;
13. A process as claimed in any one of the preceding claims, wherein Cr_8O_{21} is converted to said composite of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$) when the temperature is maintained between $400-450^\circ\text{C}$;
14. A process for manufacture of substantially pure half metallic ferromagnet chromium dioxide (CrO_2), or composites of chromium dioxide and chromium sesquioxide ($\text{CrO}_2/\text{Cr}_2\text{O}_3$), substantially as herein described in the text, examples and accompanying drawings.

Dated this 28th day of August 2002.



S. MAJUMDAR
of S. MAJUMDAR & CO.
Applicants' Agent

Abstract:

In the present invention, following a sequence of extraordinary simple steps, ferromagnetic chromium dioxide of substantially high purity has been produced. More significantly, this method is unique in a sense that it does not require pressure as a control parameter during the process of synthesis. Further, $\text{CrO}_2/\text{Cr}_2\text{O}_3$ composites have also been prepared where the fraction of insulating Cr_2O_3 in metallic CrO_2 can be easily controlled. Both CrO_2 as well as $\text{CrO}_2/\text{Cr}_2\text{O}_3$ composites are basically magnetoresistive materials and have potential for application in rapidly evolving area of Spintronics (device based on spin polarized current). Stoichiometric CrO_2 has shown 100 percent spin polarization and is therefore the best candidate for making magnetic tunnel junctions and other devices based on switching action.

The Controller of Patents,
Patent Office,
At Mumbai.



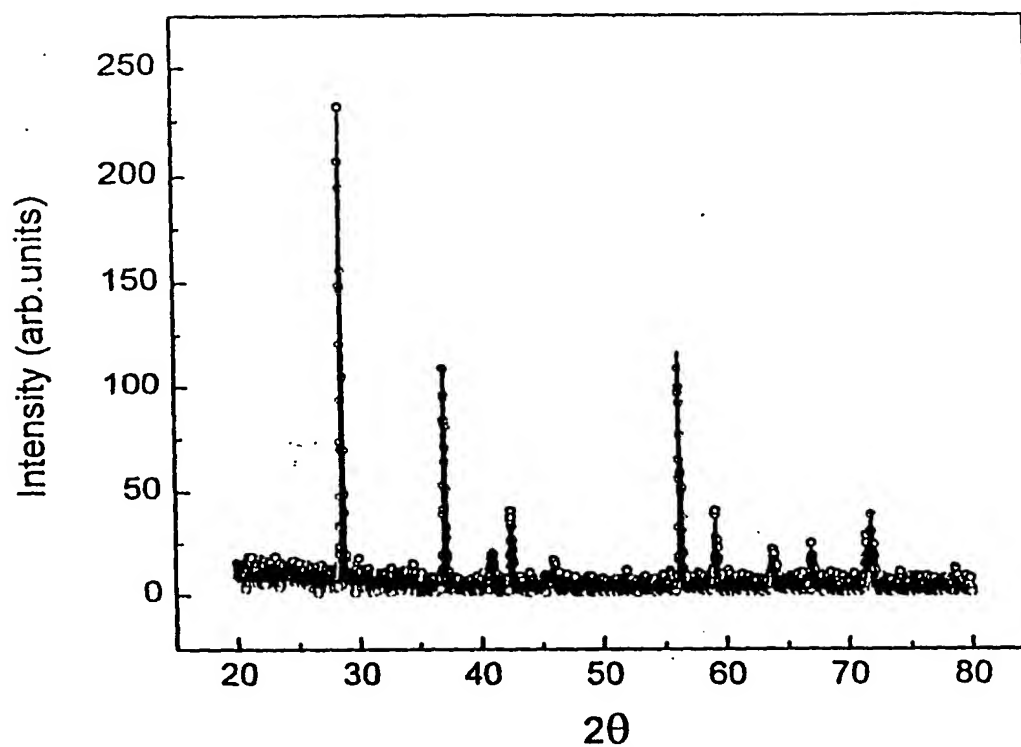


Fig.1(a): X-ray Diffraction Pattern for sample in example 1.


S. Majumdar & Company
Agent for Applicant

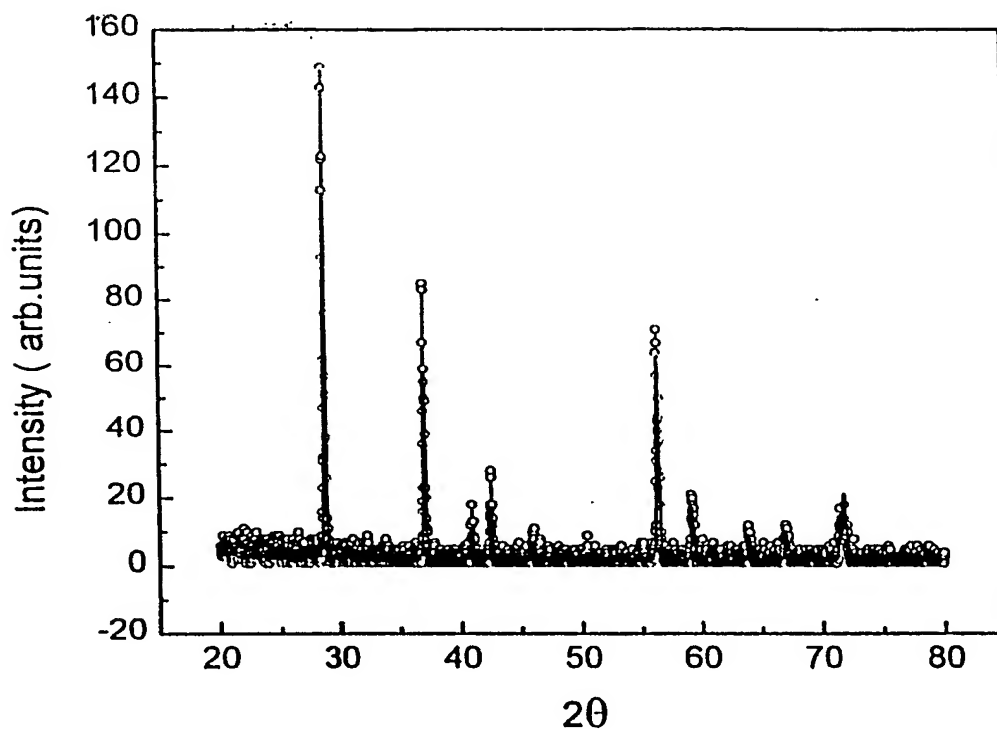


Fig.1(b): X-ray Diffraction Pattern for sample in example 2.



S. Majumdar & Company
Agent for Applicant

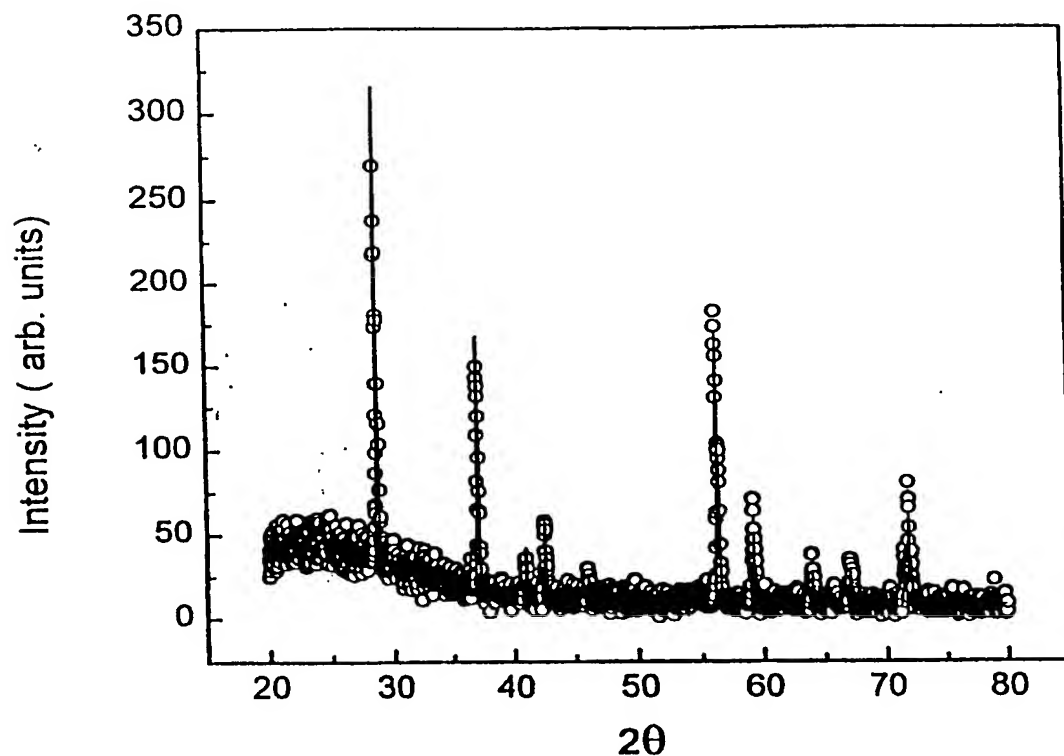


Fig.1(c): X-ray Diffraction for sample shown in example 3.

S. Majumdar & Company
Agent for Applicant

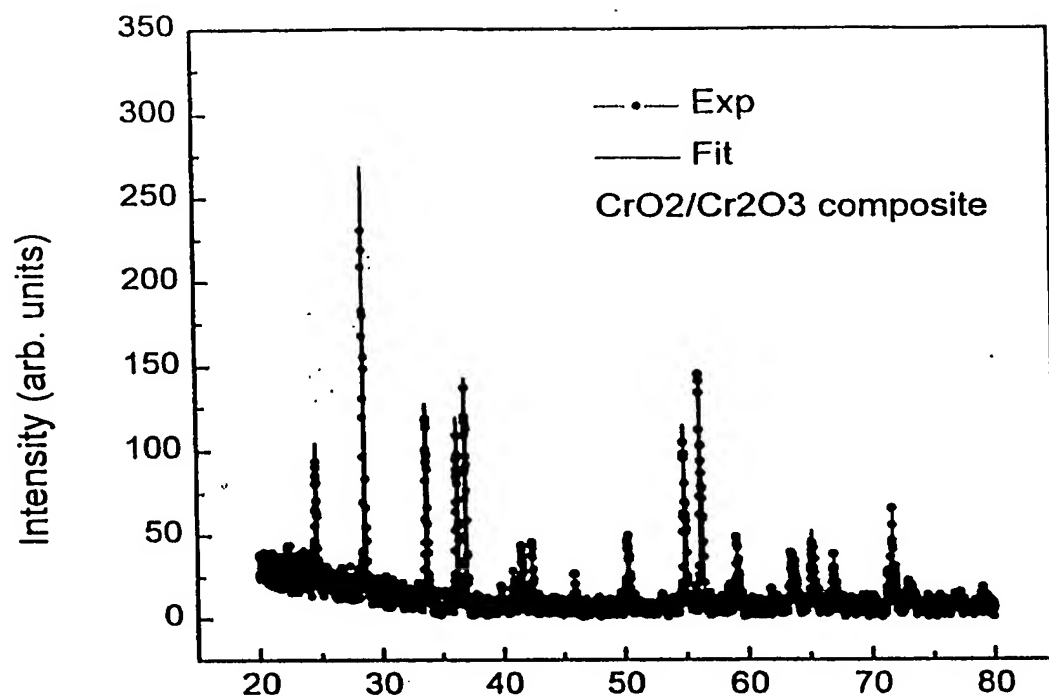


Fig.1(d): X-ray diffraction for sample given in example 4

S. Majumdar & Company
Agent for Applicant



**Fig. 2. Scanning Electron Micrograph (SEM) of the product of Example III.
The long needle shaped structures show the regular shape of CrO_2
particles.**

S. Majumdar & Company
Agent for Applicant

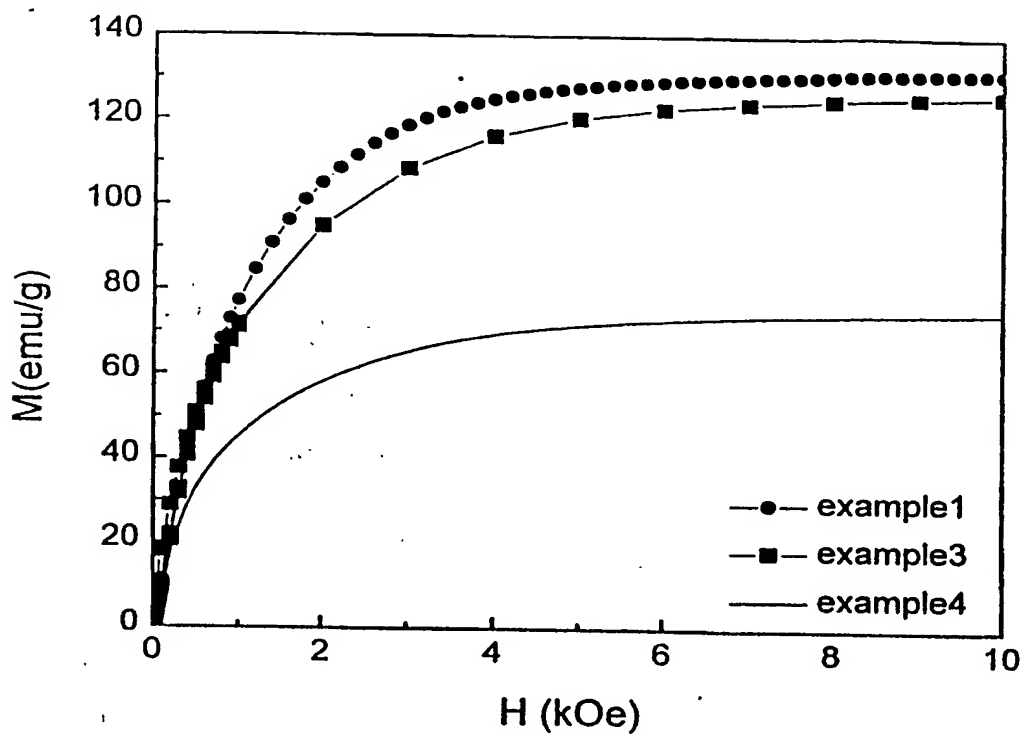


Fig.3: Magnetisation (M) as a function of magnetic field (H) at 5K


S. Majumdar & Company
Agent for Applicant